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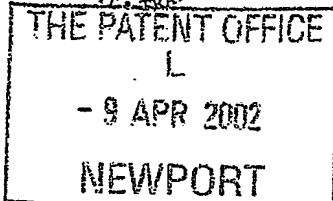
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[ADP No. 00798496001]

and

ERWAN NORMAND,
10 Glen Road,
LOCHWINNOCH,
Renfrewshire,
PA12 4HT,
United Kingdom

[ADP No. 08446650001]

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Patents ADP number (if you know it)

University of Strathclyde
McCance Building
16 Richmond Street
Glasgow G1 1XO

United Kingdom

4. Title of the invention

Semiconductor Diode Laser Spectrometer Arrangement

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Cruikshank & Fairweather
19 Royal Exchange Square
Glasgow G1 3AE

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SEMICONDUCTOR DIODE LASER SPECTROMETER ARRANGEMENT

The present invention relates to a semiconductor diode laser spectrometer arrangement and in particular an infrared semiconductor diode laser spectrometer having time resolved absorption, in which the wavenumber scale calibration is based on time to wavenumber/cm⁻¹ mapping.

Infrared absorption spectrometers are used for detecting and measuring gases. In order to achieve enhanced resolution and sensitivity, infrared semiconductor diode lasers are used extensively to provide the light to be absorbed by the measurement species. These lasers are chosen because they are relatively small, spectrally well defined, bright and tunable. Also, they potentially have a fast response time. Further advantages of these lasers over other lasers exist, some of which can be seen in spectroscopic monographs.

In remote locations and harsh environments, one of the most effective and accurate methods of trace gas sensing uses semiconductor diode laser based spectrometers. However, although gas sensing has been undertaken for some decades, in many environments it remains difficult to remotely monitor trace gas constituents. Many previous instruments have slow response times, are frequently bulky, unreliable, expensive, and require constant maintenance.

In order to retrieve precise information with known technology, remote sensing of gases usually takes place in the near and mid-infrared region of the electromagnetic spectrum, where the chemical fingerprints of most of chemical compounds lie. By near and mid-infrared, it is

meant radiation having a wavelength in the range of $1\mu\text{m}$ to $13\mu\text{m}$. This spectral region contains highly transmitting windows, so-called "atmospheric windows", which owe their transparency to the low density of strong absorption lines of CO_2 and H_2O . These atmospheric windows are of great interest for spectroscopy since the absorption lines of strongly absorbing trace molecules have similar or greater intensity than the weak lines of CO_2 and H_2O .

10 Near-infrared diode lasers produce light in the wavelength range of the vibrational overtones, about $1\mu\text{m}$ to $2.2\mu\text{m}$. These lasers have been developed mainly for the telecommunication industry. However, since the absorption

15 coefficients of the vibrational overtones are much smaller than those of the fundamental bands, the sensitivity of spectrometers that use such lasers remains limited. Thus, the sensitivity of such gas sensing apparatus rarely achieves the sub-part per billion (sub-ppb) range.

20 Mid-infrared diode lasers produce light in the wavelength range of the fundamental bands, about $3\mu\text{m}$ to $13\mu\text{m}$. These lasers have not been as technologically developed as those in the near infrared region, and hence have low single mode output power. Mid-infrared diode lasers are however used in gas sensing systems capable of achieving sub-ppb 25 sensitivity. The development of such light sources has, therefore, been wholly dedicated to spectroscopic applications.

30 Conventional mid-infrared diode lasers, principally lead salt lasers, have several disadvantages, low output power, high price, and their need to be cryogenically cooled to 77K or to even lower temperature. Thus, they require a

bulky and expensive operating system to maintain this temperature.

Recently, room temperature and high light output power
5 operation has been achieved in the mid-infrared using
quantum cascade (QC) lasers. Unlike preceding lasers, QC
lasers are unipolar semiconductor lasers that can be
designed to emit at any desired wavelength in the mid-
infrared. Replacement of lead salt lasers by QC lasers
10 provides the potential to improve both the detection
sensitivity and spectral resolution of mid-infrared
absorption spectrometers.

QC laser based spectrometers developed so far are based on
15 two main approaches. The first uses a continuous wave
(CW) operating QC laser as a "drop-in" replacement for a
lead salt laser. The second approach is to use a pulsed
QC laser in a way that mimics the use of a continuously
operating laser. In some experiments conducted by Webster
20 et al (Applied Optics LP 40, 321(2001)), the first
approach was used with one of the lead salt diodes in an
ALIAS II spectrometer being replaced by a QC laser. Test
measurements made using an ER2 aircraft platform showed
25 that the QC laser could successfully replace a lead salt
laser and was less affected by temperature instability.
However, in CW operation the laser needed to be operated
at 77K.

The second method was described originally by Whittaker et
30 al (Optics Letters 23, 219 (1998)). In this method a very
short current pulse is applied to a QC laser operating
near room temperature to provide a narrow wavelength
pulse. In this mode of operation the spectral resolution
is limited by the wavelength up-chirp. Thus in this type

of spectrometer the wavelength up-chirp is regarded as detrimental to the operation of the system.

5 The wavelength up-chirp ("effective emission linewidth") is induced by the temporal duration of the drive current/voltage pulse. By the term "effective emission linewidth", it is meant the observable/measurable spectral width (FWHM) of the emission of a semiconductor diode laser induced by an applied current/voltage pulse to its
10 electrical contacts. For example, if the duration of the pulse applied to a QC laser were of the order of 11ns, the effective emission linewidth would be of the order of 720MHz (0.024 cm^{-1}) in the spectral domain (Optics Letters 23, 219 (1998)).
15

20 In order to scan samples using a pulsed QC laser based spectrometer, the effective emission linewidth is tuned across a spectral region using a slow DC current ramp superimposed on the pulse train. This means that the resultant spectral tuning is a quadratic function of the DC current ramp injected to the laser [Optics Letter 23, 219 (1998); Applied Optics 39 6866 (2000); Applied Optics 41, 573 (2002)]. A problem with this approach is, however, that an additional step is needed in the data processing stage, to correct for the quadratic effect. In some cases, to improve the signal to noise ratio, (Optics Letters 23, 219 (1998)), a small AC current modulation signal is added to the DC ramp in order to use phase sensitive detection of the detected optical signal. Whilst adding this modulation may increase sensitivity, it requires the use of demodulation in the detection system, so rendering the system more complex. A further problem with this is that the use of a modulation inherently reduces the scan rate, since the high speed detected signals are
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demodulated to low audio frequencies signals. Hence, prior art arrangements of this type allow scan rates of only the order of tens of Hertz.

5 As can be seen, known spectrometers using semiconductor diode lasers, in particular quantum cascade (QC) lasers, have shortcomings, which limit their use for absorption spectroscopy in pulsed operation. Specifically prior art QC laser based spectrometers, where the light sources have
10 to be driven in pulsed mode operation to achieve room temperature operation, have the resolution of their effective emission linewidth determined by the temporal duration of the drive voltage/current pulse applied to its electrical contacts. The spectral resolution of those
15 spectrometers is known to be limited by the effective emission linewidth of their semiconductor diode lasers.

An object of the present invention is to obviate or mitigate at least one of the aforementioned problems.

0 According to one aspect of the invention there is provided a method for sensing gases using semiconductor diode laser spectrometer, the method comprising: applying a substantially step function electrical pulse to a semiconductor diode laser to cause the laser to output a continuous wavelength chirp; using the continuous wavelength chirp as a wavelength scan for passing through the sample, and detecting light transmitted by the sample.

By using the continuous frequency chirp of narrow intrinsic emission linewidth radiation as means for providing a wavelength scan, the spectral resolution of the spectrometer arrangement is determined by the temporal

response of the detection system rather than the temporal duration of the pulse provided by the current generator.

The duration of the pulse applied to the semiconductor diode laser may be equal to or less than 1 microsecond. The duration of the pulse may be less than the duration necessary for the optical output power to become zero after the drive pulse has been applied. The duration of the pulse may be less than the duration necessary for the centre frequency of the intrinsic emission linewidth radiation of the laser to reach a steady state.

The method may further involve varying the rate of change of reciprocal wavelength per unit time, for example by varying the amplitude of the current/voltage drive pulse.

The method may involve adjusting the wavelength scan length, for example, by varying the duration of the current/voltage drive pulse. The starting wavelength of a scan may be adjusted by varying the semiconductor diode laser temperature. This may be done using a thermoelectric heater/cooler. The temperature may also be varied by adjusting the duty cycle or the pulse repetition frequency of the pulses applied to the laser diode or pulse amplitude.

The semiconductor diode laser may output radiation having wavelengths in the region of $1\mu\text{m}$ to $14\mu\text{m}$. The spectrometer requires single mode laser radiation. This radiation may be provided by a single mode semiconductor diode laser, or by a filtered multi-longitudinal mode laser. The spectral filter must allow only single mode laser radiation to be transmitted. Preferably the semiconductor diode laser is a quantum cascade laser.

According to another aspect of the invention there is provided a semiconductor diode laser spectrometer for measuring radiation absorption by a sample, the spectrometer comprising a semiconductor diode laser; an electric pulse generator adapted to apply a substantially step function electrical pulse to the laser to cause the laser to output a continuous wavelength/frequency chirp, the chirp providing a wavelength scan for passing into the sample, and a detection system for detecting light transmitted by the sample.

The duration of the electrical pulse may be equal to or less than 1 microsecond. The duration of the electrical pulse may be less than the duration necessary for the optical output power to become zero after the drive pulse has been applied. The duration of the electrical pulse may be less than the duration necessary for the centre frequency of the intrinsic emission linewidth radiation of the laser to reach a steady state.

Means may be provided for varying the rate of change of wavelength per unit time of the chirp. The means for varying the rate of change of wavelength may comprise means for varying the amplitude of the current/voltage drive pulse.

Means may be provided for adjusting the wavelength scan length, for example by varying the duration of the electrical pulse. Means may be provided for varying a starting wavelength point of the wavelength scan. The means for varying a starting wavelength point may be operable to adjust the semiconductor diode laser base temperature. The means for adjusting the base temperature

of the semiconductor diode laser may comprise a thermoelectric heater/cooler. The means for adjusting the base temperature of the semiconductor diode laser may comprise means for adjusting the duty cycle or the pulse repetition frequency of the repeated current/voltage drive pulses applied to the electrical contacts of the laser diode. The means for adjusting the base temperature may comprise means for adjusting the pulse amplitude of the current/voltage drive pulses. The means for adjusting the base temperature may comprise means for adjusting the base DC level of the current/voltage drive pulses applied to the electrical contacts of the laser diode.

The detection system may comprise at least one detection means and at least one digitisation means. The detection system may comprise a control and acquisition system.

The amount of radiation absorbed may be determined using an amplitude measurement of radiation transmitted through the sample and an amplitude measurement of a reference pulse respectively for all spectral elements. A beam splitter may be provided to split radiation output from the laser into two components, the first component for passing through the sample and a second component that does not pass through the sample, being the reference pulse. The pulse transmitted through the sample may follow an optical path that is longer than that followed by the reference pulse.

The semiconductor diode laser may emit radiation having wavelengths in the region of $1\mu\text{m}$ to $14\mu\text{m}$. The spectrometer requires single mode laser radiation. This radiation may be provided by a single mode semiconductor diode laser, or by a filtered multi-longitudinal mode

laser. The spectral filter must allow only single mode laser radiation to be transmitted. Preferably the semiconductor diode laser is a quantum cascade laser.

5 The spectrometer arrangement may be an open path configuration wherein the gas sample is unconfined. The spectrometer arrangement may be a closed path configuration wherein the gas sample is confined in an optical cell.

10 The sample may include at least one measurement species. The sample may include a plurality of measurement species. The measurement species may be a gas. The measurement species may be an aerosol.

15 These and other aspects of the invention will now be described by way of example only and with reference to the accompanying drawings, of which:

20 Figure 1 shows computer simulated plots of emission versus wavenumber for various experimental set ups;

Figure 2 show ways in which a scanning Fourier transform spectrometer may be used to characterise semiconductor lasers;

25 Figure 3 shows plots of wavenumber versus pulse duration at various different temperatures and current amplitude;

Figure 4 shows plots of dynamic impedance and wavenumber chirp Beta;

30 Figure 5 shows experimental and computer simulated plots of the transient behaviour of the output pulse from a QC laser;

Figure 6 shows plots of voltage versus current and the light output power versus current of the QC laser;

Figure 7 shows plots of wavenumber versus temperature and duty cycle;

Figure 8 shows plots of transmission spectra of CF_2CH_2 using a black body source and a laser, recorded using the apparatus in Figure 2b;

5 Figure 9 shows higher plots of transmission spectra of CF_2CH_2 using a black body source and a laser, recorded using the apparatus in Figure 2b;

Figure 10 is a block diagram of a first spectrometer in which the invention is embodied;

10 Figure 11 shows a reference transmission spectrum of CF_2CH_2 and laser spectra with and without absorption by CF_2CH_2 using the spectrometer of Figure 10;

Figure 12 shows reference transmission spectra of CF_2CH_2 and laser spectral absorption coefficients measured using the spectrometer of Figure 10;

15 Figure 13 a reference transmission spectrum of CH_3F and a laser spectral absorption coefficient measured using the spectrometer of Figure 10;

20 Figure 14 shows the emission spectrum of a multi-longitudinal mode laser recorded using the apparatus in Figure 2a;

25 Figure 15 shows plots of part of the transmission spectrum of ammonia using a black body source and a multi-longitudinal mode laser with absorption by ammonia, these plots being recorded using the apparatus in Figure 2b;

Figure 16 shows plots of part of the transmission spectrum of ammonia using a black body source and of a multi-longitudinal mode laser with and without absorption by ammonia, recorded using the apparatus in Figure 2b;

30 Figure 17 shows simulated plots of part of the transmission spectrum of a complex molecule over part of the spectral range of a multi-longitudinal mode laser;

Figure 18 shows simulated plots of part of the transmission spectrum of a complex molecule with a spectral filter used;

5 Figure 19 shows simulated plots of part of the transmission spectrum of a complex molecule with a spectral filter used and with temperature tuning;

Figure 20 shows schematic diagrams of various methods of detecting optical pulses using the spectrometer of Figures 10 and 21;

10 Figure 21 is a block diagram of a prior art spectrometer;

Figure 22 is a block diagram of another prior art spectrometer;

Figure 23 is a block diagram of another spectrometer in which the invention is embodied, and

15 Figure 24 is a block diagram of yet another spectrometer in which the invention is embodied.

The spectrometer in which the invention is embodied advantageously uses the wavelength up-chirp or effective emission linewidth exhibited by pulsed QC and semiconductor lasers to provide a wavelength scan. Each individual pulse output by the laser provides a wavelength scan, by virtue of the wavelength up-chirp. This wavelength up-chirp is induced by a heating effect occurring for the entire duration of the applied current/voltage drive pulse. For these lasers, the wavelength up-chirp has been shown to be continuous. More specifically, under particular conditions of the electrical drive pulse shape (Optics Communications 197, 115 (2001)), the spectral behaviour of pulsed QC lasers is characterised by the fact that this wavelength up-chirp is linear with respect to time. It has further been shown that in pulsed operations the spectral behaviour of QC lasers can be mapped to the temporal definition of the

applied drive current/voltage pulse to its electrical contacts. In view of this, it is possible to map the light output temporal behaviour of a QC laser and to show it in the time domain with a photodetector.

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Figures 1a to 1g show computer simulated plots of the temporal and spectral responses for single mode and multimode semiconductor diode lasers when a square current/voltage signal is applied to their electrical contacts. For the purposes of this description, the term temporal response means the time taken for the detection system to achieve a deflection on a range proportional to an electrical signal, in the shape of a perfect step function, applied to its input. The temporal response is calculated using the usual equation for the relation between the rise time and the bandwidth of a system, i.e. temporal response = rise time = $0.35/\text{bandwidth}$.

Figures 1a and 1b show computer simulated results for the spectral behaviour at a fixed moment in time so that no chirp is observed in the spectral domain and that the represented emission linewidth is the intrinsic emission linewidth. By the term "intrinsic emission linewidth", it is meant the instantaneous observable/measurable spectral width (FWHM) of the emission. The intrinsic emission linewidth of a semiconductor diode laser is usually much smaller than the effective emission linewidth and can be difficult to quantify under pulsed operation.

Figures 1c and 1d show computer simulated results achieved on the application of a well-defined rectangular current/voltage drive pulse with a duration sufficiently long so that a chirp is observed towards longer wavelength. As mentioned previously, this chirp arises

from heating effects induced by the drive pulse. The amplitude decay that goes with this chirp is caused by the reduced efficiency of lasing action as the heating increases. The effect of the wavelength chirp can be seen more clearly in Figures 1e and 1f. A computer simulation of the temporal behaviour of the emission is shown in Figure 1g. Note that since the amplitude decay of the chirp decreases with time, the temporal response is a mirror image of that in the spectral domain.

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Figures 2a and 2b show two possible arrangements by which a continuous scanning infrared Fourier transform spectrometer may be used to characterise the spectral output behaviour of semiconductor diode lasers. Experimental measurements of the wavelength chirp are carried out using the arrangement Figure 2a. The results are shown in Figures 3-7.

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Figure 3a is a plot of wavenumber chirp as a function of the temporal duration of the applied current pulse (fixed amplitude 4.2 A) for a range of substrate temperatures. The results indicate that the rate of tuning, over the temperature range investigated, is insensitive to temperature. From this plot the rate of change of wavenumber as a function of time β can be determined empirically. To vary β , the amplitude of the current/voltage pulse must be altered, as illustrated in Figure 3b. From this, it can be seen that irrespective of the applied current, over the range of currents used, β is linear in nature. β is related to the power dissipated inside the laser diode and the linear variation in β arises from the fact that the QC laser exhibits a dynamic impedance, as shown in Figure 4a, which results in a linear power dissipation over the current range used, see

Figure 4b. It should be noted that the value of β is determined over the temporal range for which the output shows no transient behaviour, see Figure 4c. The limiting values of β are defined, at the lower end, by the current/voltage amplitude necessary to achieve a usable output power and at the upper end, by the current/voltage amplitude that induces a reduction in the output power, see Figure 6.

The starting wavenumber of the wavenumber chirp is influenced by both the substrate temperature of the QC laser and the duty cycle of the applied current/voltage pulses as shown in Figures 7a and 7b. Hence, by varying the substrate temperature and/or the duty cycle, the starting wavenumber can be altered.

The linear wavenumber down-chirp can be exploited to make spectral measurements using the experimental arrangement shown in Figure 2b. Typical spectra are shown in Figures 8 and 9. In Figure 8 a comparison is made between a spectrum recorded with a blackbody source (upper trace) and a spectrum recorded using a QC laser (lower trace). Figure 9 show the same information using a much higher resolution FTS. This comparison of spectra recorded with a resolution of 0.0015 cm^{-1} (45 MHz) using a blackbody source and a wavelength chirped QC laser shows that the instantaneous linewidth of the QC laser must be less than the instrumental resolution of the FTS.

The linearity of the wavenumber chirp as a function of time allows the construction of a high speed, sub-microsecond, semiconductor diode laser absorption spectrometer. Figure 10 shows arrangements 1a and 1b for measuring the radiation absorbed by a species, i.e a gas

sample. The spectrometer determines the absorption coefficient of a species by measuring the ratio of the intensity of the light transmitted through an empty cell, I_0 and that transmitted through a cell containing the absorbing species, I_a . These intensities are related through the Beer Lambert Law $I_a = I_0 \exp(-\alpha L)$, with α the absorption coefficient and L the optical path length. It should be noted that α is a function of wavenumber and is independent of the intensity at low intensities of the incident radiation.

The spectrometer arrangement 1 is a closed optical cell (confined gas) configuration and comprises a current/voltage drive pulse generator 19 that is connected to an input of a laser 20. The pulse generator 19 is operable to apply substantially rectangular pulses to the laser 20. In this case, the laser 20 is a single mode semiconductor diode quantum cascade laser (QC laser).

The laser 20 is housed in a Peltier temperature controlled enclosure (not shown). The Peltier element is controlled by a thermoelectric controller 28. Connected to the laser enclosure is a compressor and pump unit 11, which is used to cool/heat fluid and circulate that fluid into the hollow housing of the diode laser enclosure 20. This enables the laser element to be operated over a wider temperature range than is possible using solely the Peltier element.

On an optical path from the laser 20 output is an optional spectral filter 15, for example a small grating monochromator, which may be used to provide a single mode laser output if a multi-longitudinal mode laser is used. The single mode radiation can traverse two possible

optical paths, 16a and 16b. If only a single detector is used then the beam splitter 21 is replaced by a mirror. Otherwise, the single mode output is split into two substantially perpendicular beams 16a and 16b using a suitable beamsplitter, for example a germanium beam splitter for laser radiation at wavelengths close to $10\mu\text{m}$. However, it will be appreciated that any other suitable splitter could be used.

In the case of the use of a single detector 23, (the single beam method, SBM) only optical path 16a is used, and both I_o and I_a are measured using a single absorption cell 17. The beam output from the cells 17 is directed to a detection system. This comprises a detector 23 for detecting a light pulse output from the gas cell 17. Connected to the detector 23 is a digitiser 12. The measurement made using the evacuated cell 17, I_o , is digitised by the digitiser 12, and is stored by the control and acquisition system 10. I_a is measured when the cell 17 is filled with the gas sample 13, and subsequently digitised by the digitiser 12.

When two detectors, 23 and 24, are used, (the dual beam method, DBM) on an optical path of beam 16a is provided an optical cell 17 in which is disposed gas sample 13. On the optical path of beam 16b is an optical reference cell 18. This has identical characteristics to cell 17 but is evacuated and sealed. The beams output from the gas and reference cells 17 and 18 respectively are directed to a detection system. This comprises a first detector 23 for detecting an absorbed light pulse output from the gas cell 17 and a second detector 24 for detecting the background light pulse output from the reference cell 18. Connected to the first detector is a first digitiser 12. Likewise,

connected to the second detector is a second digitiser 14. Because of the sensitivity of laser spectrometers to the quality of the optical windows, the use of identical optical cells 17 and 18, allows the main effects of mismatched windows, etalon fringes, to be reduced.

In both the SBM and DBM methods the value of the absorption coefficient is determined using I_o and I_a in the Beer - Lambert equation.

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Control of the overall system 1 is provided by a control and acquisition system 10, which is connected to each of the current/voltage drive pulse generator 19, the spectral filter 15, the pump and compressor 11 and the first and second digitisers 12 and 14 respectively. The control system 10 is operable to set the amplitude and duration of the pulse applied to the laser input and monitor the resultant outputs detected from the gas and reference cells 17 and 18 respectively. The control system 10 is also operable to determine the ratio I_o/I_a . This is done using Beer Lambert's Law, which may be written as $\alpha L = \ln(I_o/I_a)$. In the limit of small absorption, this may be approximated as $I_o/I_a = 1 + \alpha L$. Hence, since the path length through the gas sample is known the measurement of the wavenumber dependent absorption cross-section α can be determined directly.

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In both embodiments of the spectrometer of Figure 10, the SBM and the DBM, the background light pulse with amplitude I_o and an absorbed light pulse with amplitude I_a , each have the same distance to travel to the detection system. Hence in the DBM case, providing that the optical paths 16a and 16b are identical, both pulses arrive at the detectors 23 and 24 at the same time. In this way, using

Beer Lambert's law, only the absorption is directly sensed for each individual scan via the use of the ratio (I_o/I_a).

5 In use, the current/voltage drive pulse generator 19 generates a plurality of substantially rectangular pulses that are applied to the input of the laser 20. More specifically, the generator 19 provides a train of fixed amplitude sub-microsecond duration rectangular current drive pulses. This causes a fast laser heating effect and
10 hence a continuous wavelength up-chirp of the emitted semiconductor diode laser radiation at a rate in time β . As discussed previously, the fast laser heating caused by the sub-microsecond rectangular current pulses is such that for each pulse emitted from the laser 20, the chirp
15 is a continuous linear spectral variation from short to long wavelength. This is defined as a continuous spectral or wavelength scan.

20 The potential of the spectrometer arrangement shown in Figure 10 to make measurements is illustrated in Figure 11, in which a sample of 1,1 difluoroethylene (CF_2CH_2) is placed in the sample cell 17, and I_o and I_a are recorded using the SBM method using a single mode distributed feedback (DFB) laser without a spectral Filter 15. The
25 upper trace in Figure 11 shows the CF_2CH_2 spectrum recorded using the arrangement in Figure 2b, with a blackbody source replacing the QC laser. The lower two traces show both I_o and I_a . From this spectrum, it is evident that there is a strong correlation between the
30 absorption features recorded in the black body absorption spectrum and those using the single beam version of spectrometer 10. The wavelength up-chirp as a function of time means that the inverse wavelength, the wavenumber/cm⁻¹, decreases as a function of time.

The wavelength range over which the chirp-induced scan occurs is sufficient to allow an identification of the chemical fingerprint of the gas to be recorded, see Figure 5 12 and the arrows on Figure 11. The upper trace in Figure 12 shows the resolution dependence of CF_2CH_2 spectrum recorded using the arrangement in Figure 2b, with a blackbody source replacing the QC laser. The spectrum recorded with a resolution of 0.025 cm^{-1} exhibits a 10 similar resolution to the absorption cross sections recorded using the SBM method of Figure 10, which are shown in the lower half of the figure. This effective resolution may be checked by the use of nitrogen pressure broadening of the absorption lines of the sample gas. Use 15 of this method gave a value for the resolution of the spectra in the lower half of Figure 12 of about 0.03 cm^{-1} . These absorption cross sections are derived from the ratio of I_0/I_a using the Beer-Lambert law as described previously. The pressure dependence of these absorption 20 cross sections is clearly seen, and the chemical fingerprint (or signature) is readily identified even at the lowest pressure used in the cell. This demonstrates that the SBM spectrometer of Figure 10 is capable of ppb sensitivity with absorption path lengths of less than 10m. 25 Hence with easily achievable optical path lengths of several hundreds metres it would possible to reach the sub-ppb range when detecting different species within a sample. This is possible because semiconductor diode lasers such as QC lasers have a light output power reaching several watts under pulsed operations.

The main differences between the structure of the three absorption features as seen in the spectral and temporal domain are associated with ringing effects, which are

usually caused by the electronic signal processing that occurs in the detection system. These can, however, be eliminated using proper electrical signal transmission lines. The remaining differences associated with the resolution of the FTS spectrum and the direct absorption detection of spectrometer 1 could largely be eliminated if the bandwidth of the detection system were to be increased from 100MHz to 500MHz.

Figure 13 shows spectra in which a sample of methyl fluoride (CH_3F) is placed in the sample cell 17. The upper trace in Figure 13 shows the CH_3F spectrum recorded using the arrangement in Figure 2b, with a blackbody source replacing the QC laser, a resolution of 0.025 cm^{-1} . The lower trace in Figure 13 shows the absorption cross section of a sample of methyl fluoride recorded using the SBM method. The spectrum of this molecule is less complex than that of CF_2CH_2 and hence only one absorption feature occurs within the tuning range of the pulsed laser. The effective resolution of the absorption cross section may be seen to be approximately 0.025 cm^{-1} .

The replacement of a single mode QC laser, such as a distributed feedback (DFB) QC laser, by a multi-longitudinal mode laser brings both advantages and disadvantages. The principal advantage is that it widens the effective tuning range of the spectrometer as shown schematically in Figures 1a and 1b and experimentally by comparing the temperature tuning range of a single mode distributed feedback QC laser shown in Figure 7 with the wavenumber/ cm^{-1} range covered in the multimode-longitudinal mode spectrum shown in Figure 14 recorded using the Fourier transform spectrometer system of Figure 2b. The use of such a laser is analogous to that of a step

separation of the spectra and also the identification of the wavenumber/cm⁻¹ region in which they occur, as shown schematically in Figure 18. However, if the tuning of each mode provided by the wavenumber down-chirp were to be 5 greater than the longitudinal mode spacing then partial overlapping of the spectra would still occur.

If the spectrum of the multi-longitudinal mode laser were to be contaminated by the occurrence of off axis modes of the laser the spectral filtering method described would 10 become very difficult to implement. This is owing to the close wavenumber/cm⁻¹ spacing between off axis (transverse) modes which makes it extremely difficult to design a suitable efficient broad-band spectral filter.

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The final advantage of the use of a multimode laser is the possibility of using a combination of mode section and temperature tuning of individual modes to achieve complete tuning within the usable intensity low and high wavenumber modes. (gain envelope) of the laser. This is shown schematically in Figure 19. Further details of the 25 operation of the spectrometer are considered below.

25

30

By combining the sub-microsecond pulsed signal generation operation and the detection arrangement within the spectrometer arrangement 1, the spectral resolution of the spectrometer 1 is not limited by the effective emission linewidth of the laser 20. Instead the spectral resolution is mainly limited by the temporal response of the detection system. This is because the number of pixels (a pixel corresponds to a given time interval) into which the spectrum can be recorded within the wavelength chirp is limited by this response. Note that the rate of this chirp is governed by the parameter β .

5 In these simulations, it has been assumed that the spectrometer of Figure 10 uses a 256ns duration current/voltage pulse to exploit the wavelength up-chirp, and that the spectrometer of Figure 21 uses a 5ns duration current/voltage pulse (see: Applied Optics 41, 573 (2002)). The centre frequency of this effective emission linewidth of approximately 0.02 cm^{-1} is subsequently continuously tuned in a non-linear manner over a 0.75 cm^{-1} 10 spectral range starting from 992.3 cm^{-1} . For a similar current amplitude to that used for spectrometer of Figure 21 the spectrometer of Figure 10 would have a parameter β of approximately $-5.9 \times 10^{-3} \text{ cm}^1 / \text{ns}$. This would give rise to a total linear wavelength up-chirp of 1.5 cm^{-1} in 256ns.

15 As an example, if the complete detection system of the spectrometer of Figure 10 were to consist of a 500MHz bandwidth detection system and 2Gs/s digitiser, the overall temporal response would be equivalent to a 20 wavenumber resolution of 0.004 cm^{-1} . This would be an improvement of factor 5, over the system of Figure 21.

25 Method 1 allows the multiplex advantage to be obtained, since the entire spectral region is recorded within each individual or single pulse, whereas in method 2 only a single spectral element may be recorded during a single pulse. Hence if the same number of sampling points, n , is recorded, eg $n=512$ which is the maximum number possible in method 2 (see: Applied Optics 41, 573 (2002)), the theoretical improvement in signal to noise achievable in 30 method 1 should be \sqrt{n} , which for 512 point is a factor of about 22.

the absorption cell, 16a (the signal beam), and to the evacuated reference cell, 16b (the reference beam), is required, the DBM method 1b, two separate cells are needed. The DBM scheme has the advantage of minimising the long and short term effects of drift.

A single absorption cell may be used within the spectrometer for the same purpose as 1b in Figure 10 if the signal and reference beams traverse different optical paths through the same absorption cell 17. This option is shown in Figure 23 as arrangement 1c.

If the path length of the signal path, 16a, is L_a , and that of the reference path 16b is L_b , then in order to minimise absorption in the reference path 16b L_a must be much greater than L_b ($L_a \gg L_b$). The modified Beer-Lambert expression required for arrangement 1c may be derived as follows: for the signal path, $I_a = I_0 \exp(-\alpha L_a)$ and for the reference path $I_b = I_0 \exp(-\alpha L_b)$, hence $\ln(I_a/I_b) = -\alpha(L_a - L_b)$, or in the form derived previously for arrangement 1b, $-\alpha(L_a - L_b) = \alpha \Delta L = \ln(I_b/I_a)$.

In arrangement 1c the transit time difference between both pulses is chosen to be less than the wavelength up-chirp time or current/voltage drive pulse duration. Therefore, background light pulse arrives at detector 24 in advance of the arrival of the signal pulse at detector 23.

The outputs from the digitisers 12 and 14 is recorded, to enable the control acquisition circuit 10 to ratio them to provide I_0/I_a as detailed previously. An advantage of the spectrometer of arrangement 1c of Figure 23 is that fewer optical elements are used than in the first embodiment, arrangement 1b of Figure 10, e.g. no reference cell. This

reduces the overall size and weight of the spectrometer arrangement.

Arrangement 1d of Figure 23 shows a modification of arrangement 1c in which only a single detector is used. The absorption path difference is identical to that of arrangement 1c, namely $\Delta L = (L_a - L_b)$. When a pulse train is incident on the beamsplitter of Figure 23, the action of the beamsplitter is to split each individual pulse in the pulse train into two components. Any one pulse from the pulse train that follows optical path 16a has a companion pulse that follows optical path 16c. This has important consequences when considering the detection of I_c and I_a by the single detector arrangement 1d. To compute the ratio of I_c to I_a the signals corresponding to I_c and I_a must be recorded separately and then processed in the manner described for the SB mode of operation in Figure 10, embodiment 1b. This means that a pulse corresponding to I_a cannot arrive at the detector until its companion pulse corresponding to I_c has been digitised by digitiser 12 and stored by the control and acquisition system 10. The next pulse associated with I_c , however, cannot arrive at the detector, before the previous I_a pulse has been digitised by digitiser 12 and stored by the control and acquisition system 10. Thus, the difference in optical path length and hence transit time, between optical path 16a and optical path 16c must be greater than the distance defined by pulse temporal duration (speed of light $\times t_p$) but less than the distance defined by the pulse repetition time (speed of light $\times t_{rep}$).

In use, the current/voltage drive pulse generator 19 of Figure 23 generates a plurality of substantially rectangular pulses that are applied to the input of the laser 20. More specifically, the generator 19 provides a train of fixed amplitude sub-microsecond duration rectangular current drive pulses. This causes a fast laser heating effect and hence a continuous wavelength up-chirp of the emitted semiconductor diode laser radiation at a rate in time β . As discussed previously, the fast laser heating caused by the sub-microsecond rectangular current pulses is such that for each pulse emitted from the laser 20, the chirp is a continuous linear spectral variation from short to long wavelength. This is defined as a continuous spectral or wavelength scan.

Many measurements of atmospheric trace gases are made using open path (unconfined gas) arrangements, i.e. the spectrometer contains no gas cell. In Figure 24, arrangement 1e, a schematic diagram of such a possible spectrometer arrangement is given. Such a spectrometer could be used, for example, as shown in arrangement 1e of Figure 24, for monitoring the exhaust plume 40 of an engine. The arrangement of the optical components up to and including the beamsplitter 21 is identical to that of the previous embodiments 1a, 1b (Figure 10), and 1c and 1d (Figure 23). Opposite the filter 15 and on the optical path of beam 16a is a cube-corner retro-reflector 39 that is positioned in use so that the gas to be investigated is between the filter 15 and the reflector 39. Light reflected from the reflector 39 is directed back, through the gas towards the detection system. In contrast, the reference beam 16b is transmitted in a direction perpendicular to beam 16a through a much shorter optical

path towards another reflector, which reflects it toward the detection system.

5 The detection system is the DBM arrangement of embodiments 1b (Figure 10) and 1c (Figure 23). Furthermore, for the purposes of simplification in Figure 24, the following components, which are not shown, are included in system 40: a control and acquisition system 10, pump and compressor 11, thermoelectric controller 28 and pulse 10 current driver 19. The functionality of these components is the same as previously described.

15 In use of the spectrometer of Figure 24, a stream of current pulses is applied to the laser 20, which emits light that is subsequently passed through the filter 15, thereby to produce a suitable output. The light pulse to be absorbed 16a then travels through the exhaust plume 40 and is reflected by the retro-reflector 39, returning through the exhaust plume 40 to the spectrometer 1e. In 20 this way, the beam 16a makes two passes through the gas. The reflected pulse 16a is then focussed onto detector 23. The background pulse of light 16b, which is focussed onto detector 24, travels via a much shorter optical path than that of the signal pulse, 16a. Hence, the transit time of 25 the reference pulse 16b is less than that of the signal pulse 16a, so that the background pulse 16b arrives at the detector 24 before the signal pulse 16a at detector 23, when both the time measurements are made relative to that of an initial trigger pulse. Since the digitisers 12 and 30 14 can each be delayed with respect to one another, each of the detected pulse components 16a and 16b are recorded such that the control and acquisition system 10, which is incorporated in detection system will ratio them to generate I_0/I_a .

Arrangement 1f in Figure 24 is a modification of embodiment 1e requiring the use of a single detector. This is similar to the closed path arrangements shown in Figure 23. In order to separate the arrival of the signal pulse 16a and the background pulse 16b at the detector 23, the transit time difference between the pulses must be greater than that of the wavelength up-chirp time or current/voltage drive pulse duration. As in embodiment 1d, since the digitiser 12 records both detected pulses 16a and 16b on the same channel, they are then separated within the digitiser 12 and processed such that the control and acquisition system 10 can ratio them generating I_0/I_a .

The spectrometer in which the invention is embodied exploits the linear wavelength up-chirp of the intrinsic emission linewidth that occurs on a sub-microsecond time scale and therefore is able to operate a scan repetition frequency (PRF) of as high as 1MHz. This potential gain of speed, which is an improvement of several orders of magnitude compared to prior art, would allow the present system to fully exploit the multiplex capabilities advantages by, for example, achieving real time measurements to study processes such as fast chemical reactions (i.e. such as Free Radicals or real time atmospheric fluctuations) or by averaging a high number of scans n to gain in noise performances by a factor of \sqrt{n} .

Various modifications may be made to the arrangements as hereinbefore described without departing from the spirit and scope of the invention. For example, it should be understood that the present spectrometer arrangement is fully capable of using an even faster detection system

than that detailed; hence increasing further the available resolution. In a further variation, the substrate temperature of the laser could be changed. This could be done by varying the repetition rate of the applied sub-microsecond rectangular current pulse. In an alternative variation the substrate temperature can be varied by varying the base DC level of the sub-microsecond duration rectangular current drive pulses applied to the electrical contacts of the semiconductor diode laser.

10

In the embodiments detailed, the optical beam splitting means have been described as being an optical beam splitter however, they may instead be a dichroic mirror or other similar arrangement.

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It should be further understood that several semiconductor diode lasers could be implemented in the spectrometer arrangement in which the invention is embodied to achieve simultaneous measurements of different species. Further, the samples to be measured are hereinbefore described as gases but may alternatively be aerosols.

20

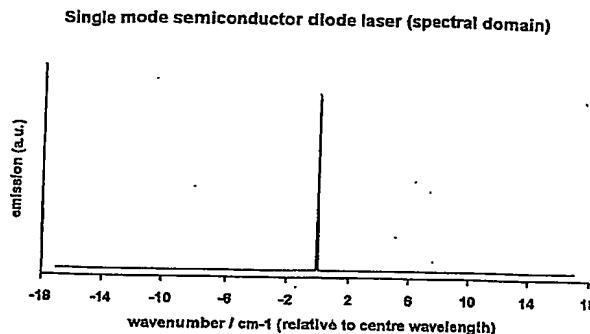


Figure 1a

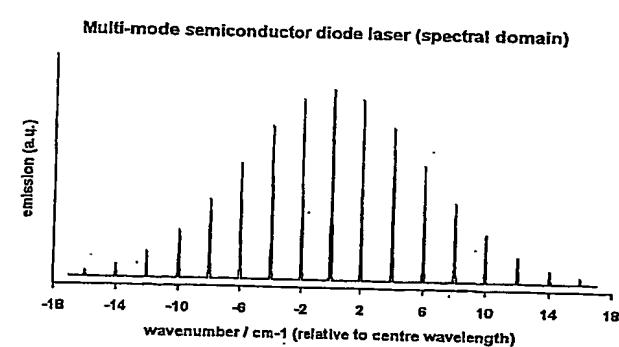


Figure 1b

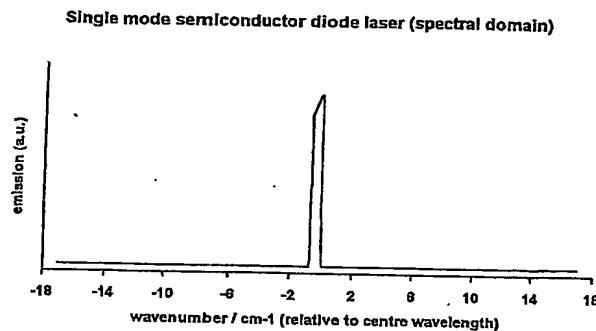


Figure 1c

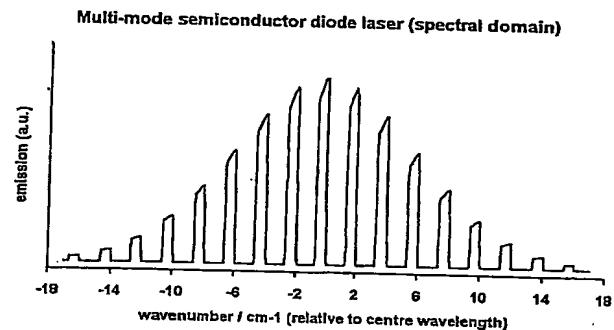


Figure 1d

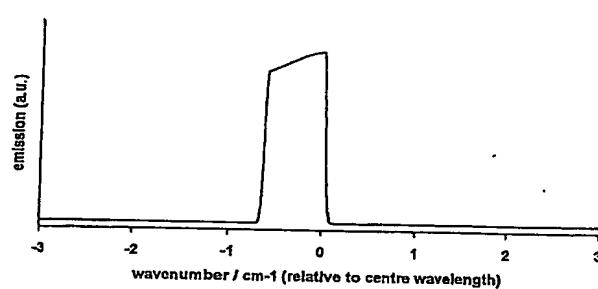


Figure 1e

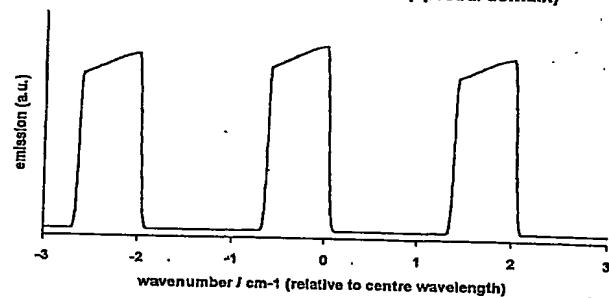


Figure 1f

Photo detector response (temporal domain)

time / ns (relative to trigger)

Figure 1g

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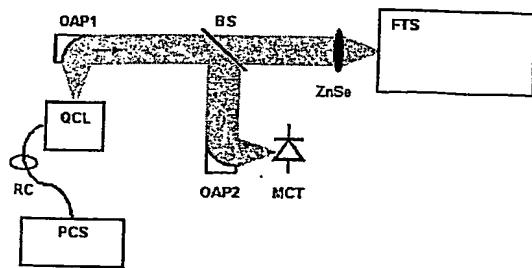


Figure 2a

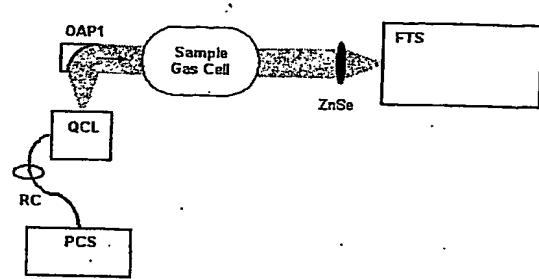


Figure 2b

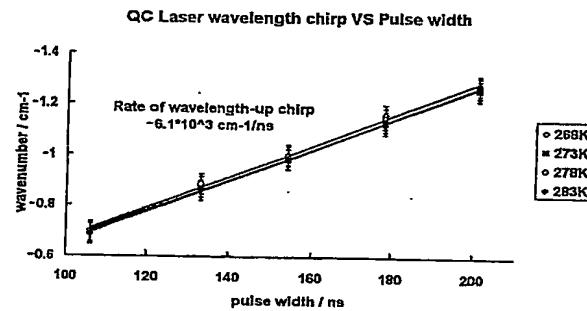


Figure 3a

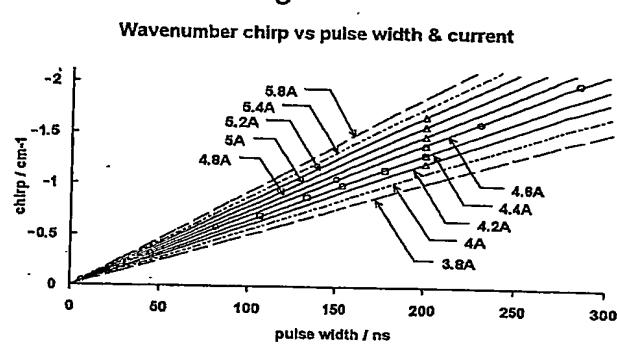


Figure 3b

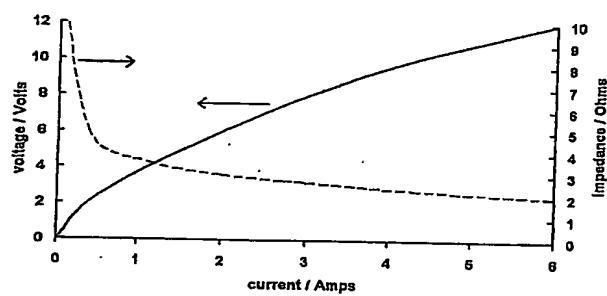


Figure 4a

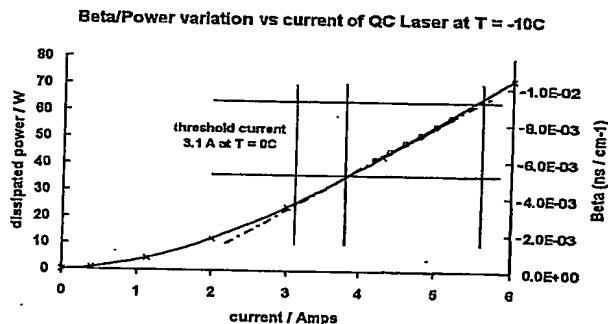


Figure 4b

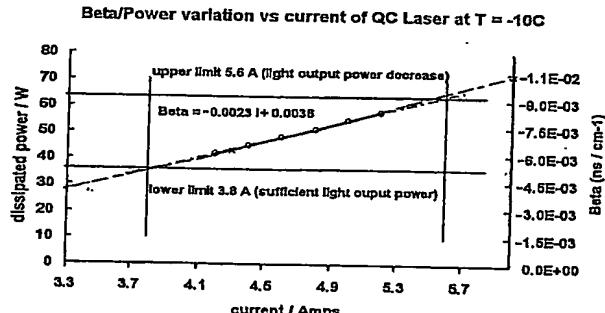


Figure 4c

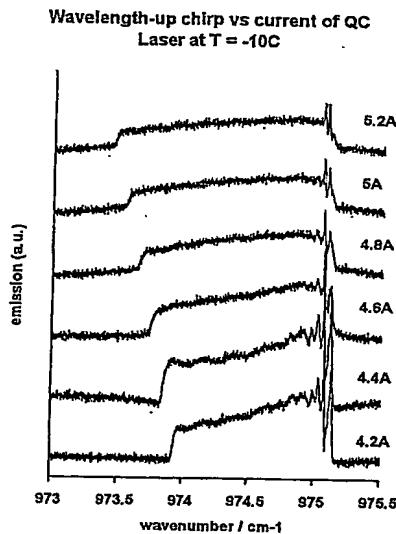


Figure 5a

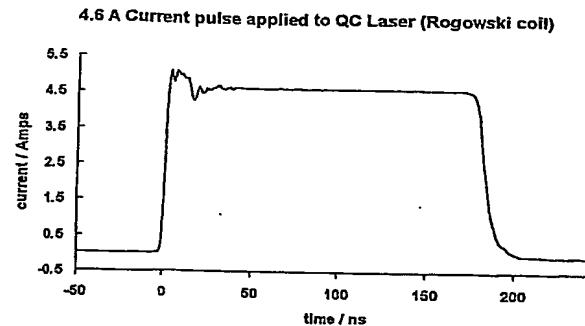


Figure 5b

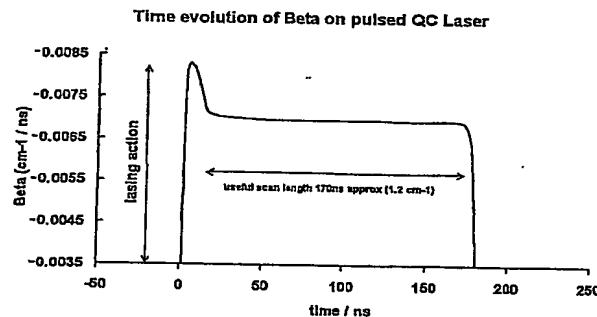


Figure 5c

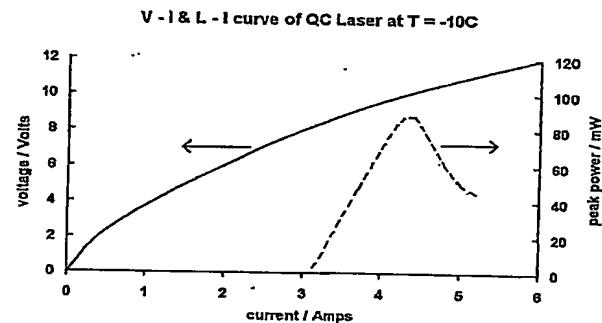


Figure 6

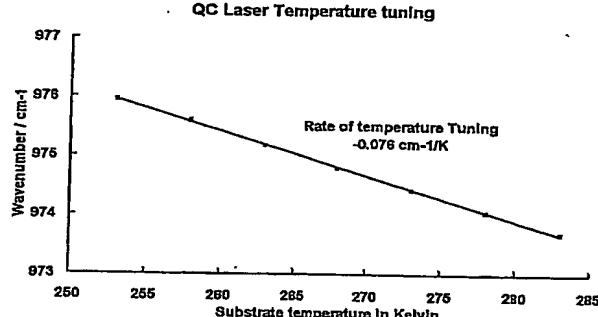


Figure 7a

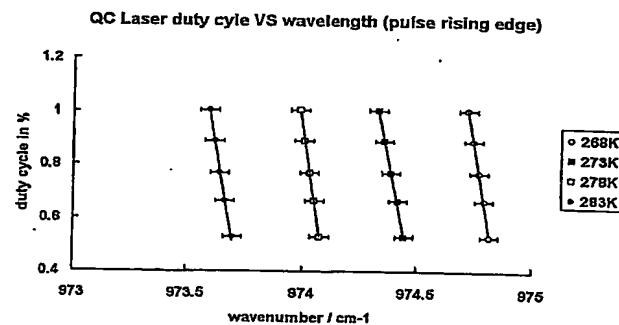


Figure 7b

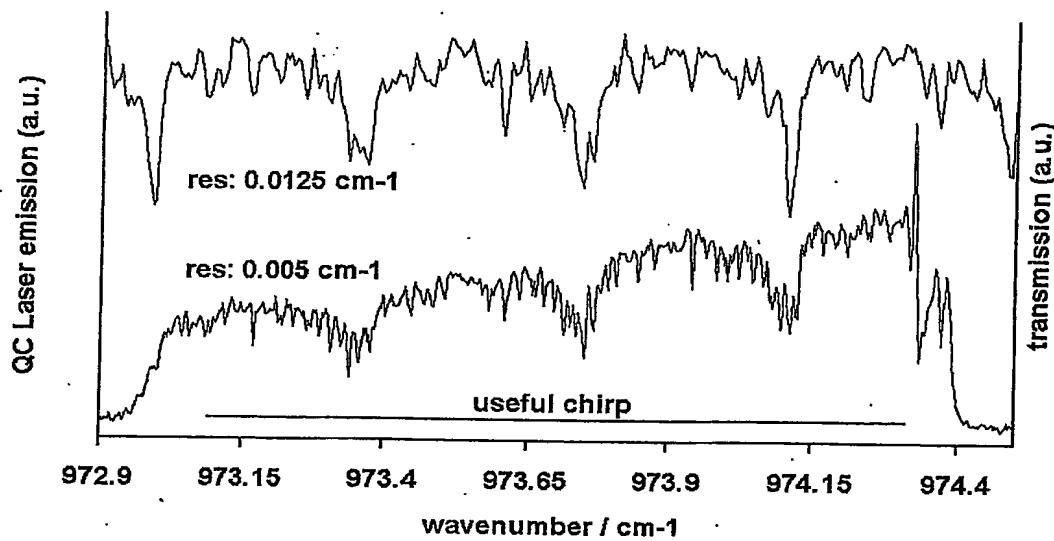
Single mode QC Laser: absorbed by CF₂-CH₂ (spectral domain)

Figure 8

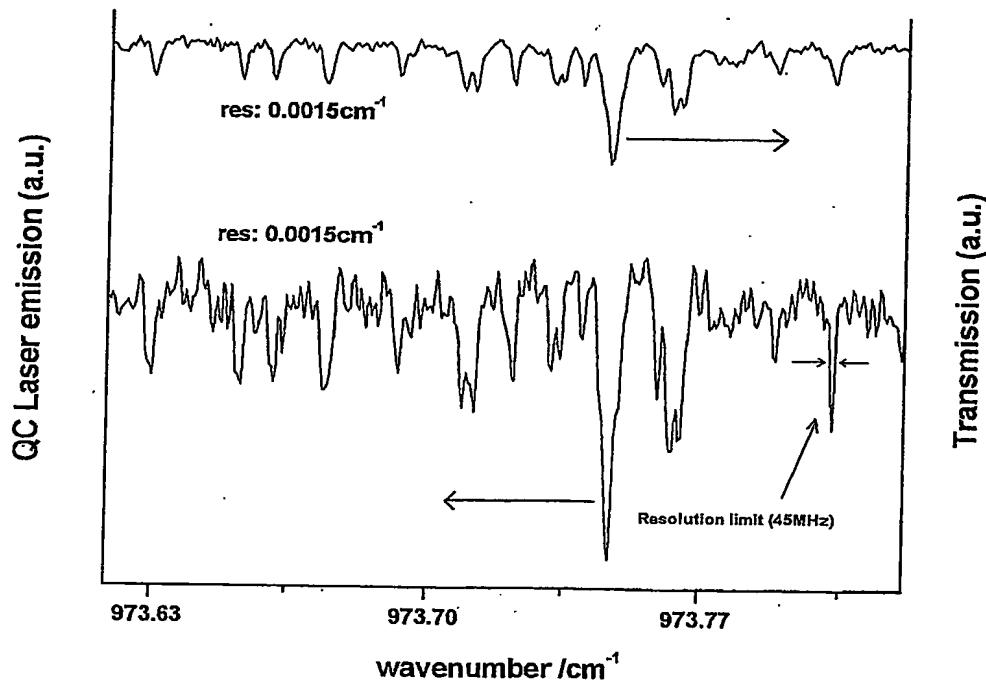
Single mode QC Laser: absorbed by CF₂-CH₂ (spectral domain)

Figure 9

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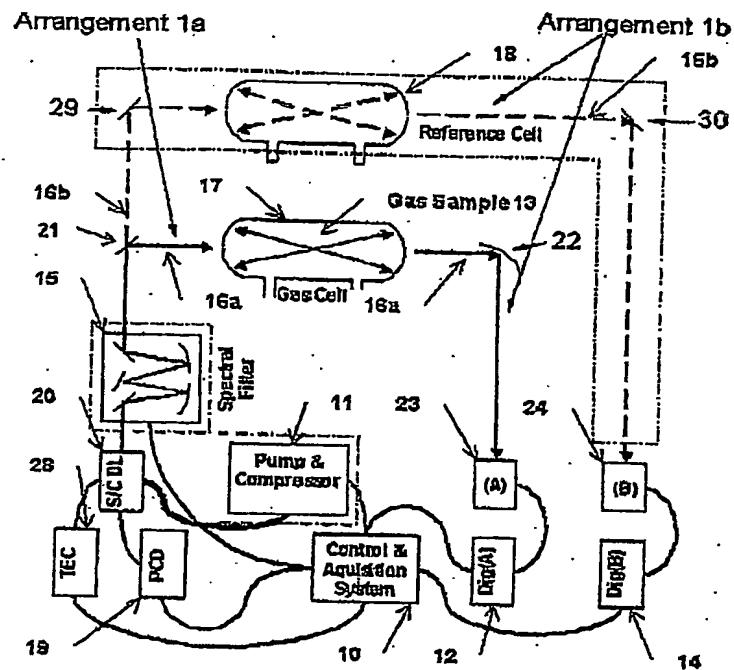


Figure 10

Photodetector response (Bkg & Absorbed- CF_2CH_2)

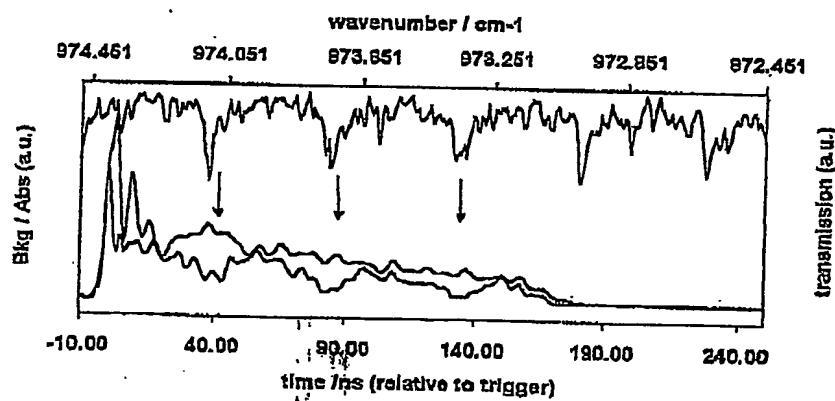


Figure 11

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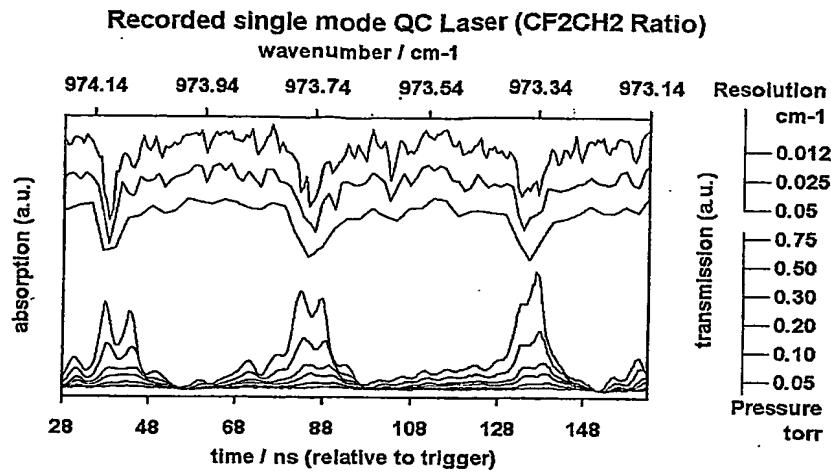


Figure 12

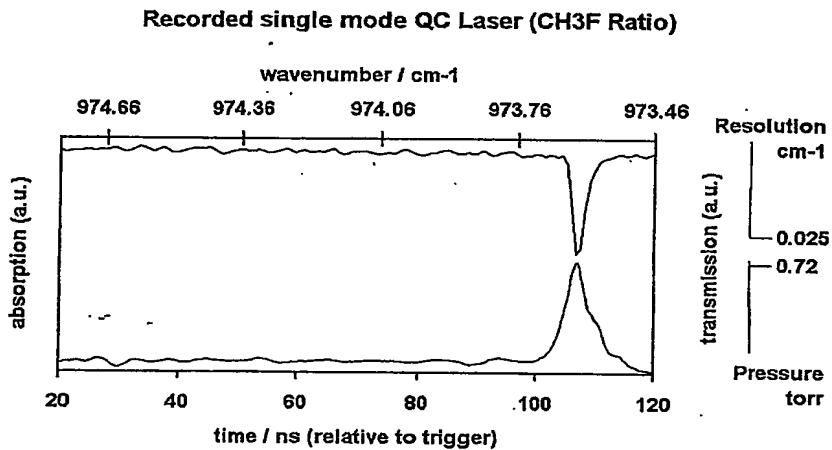


Figure 13

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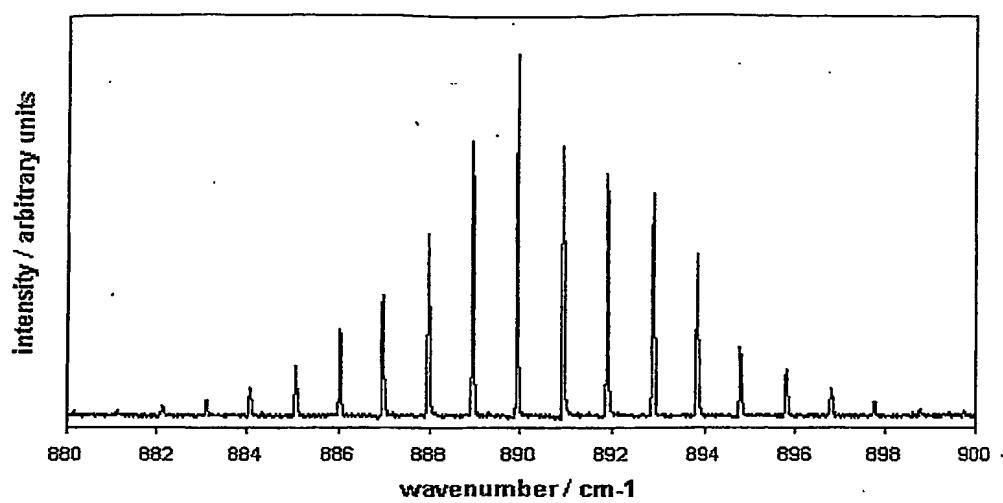


Figure 14

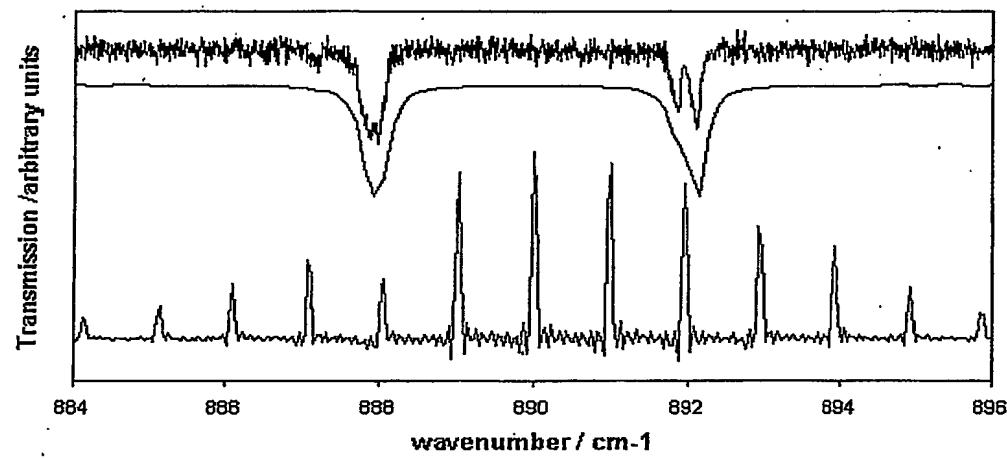


Figure 15

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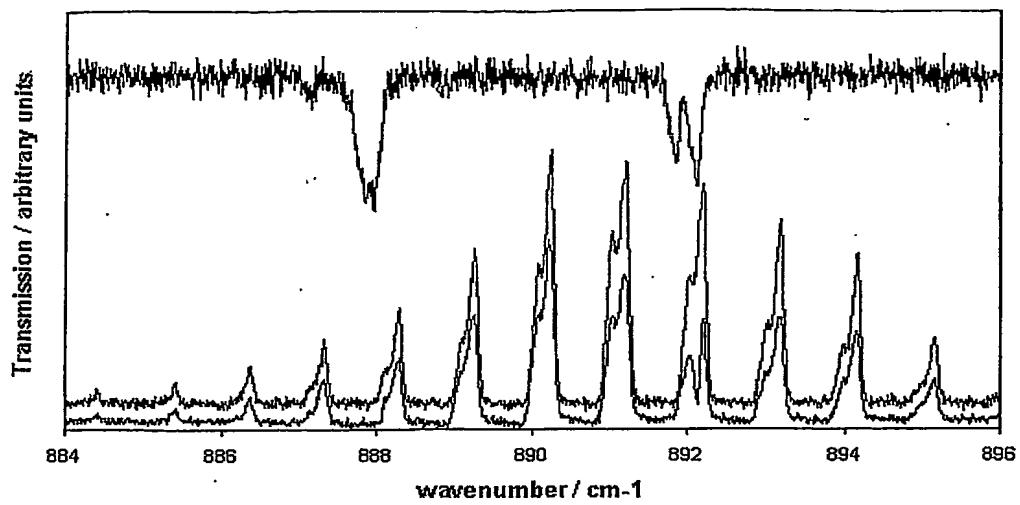


Figure 16a

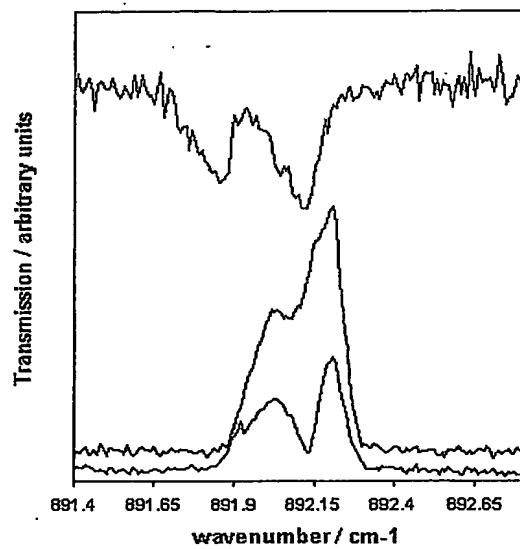


Figure 16b

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**Multi-mode semiconductor diode laser & Sample Gas
(spectral domain)**

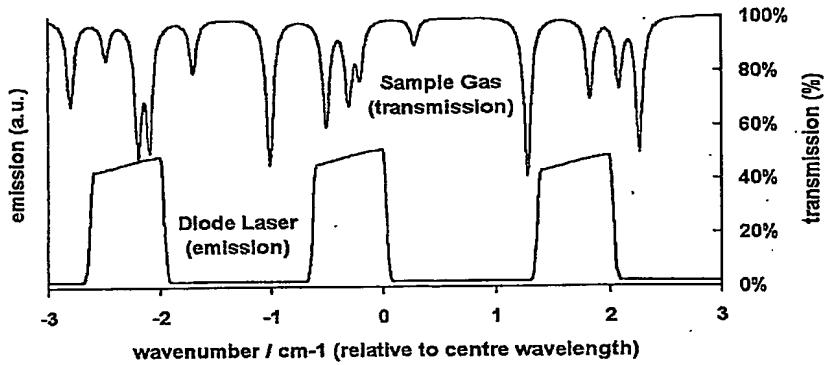


Figure 17a

**Multi-mode semiconductor diode laser: absorbed
(spectral domain)**

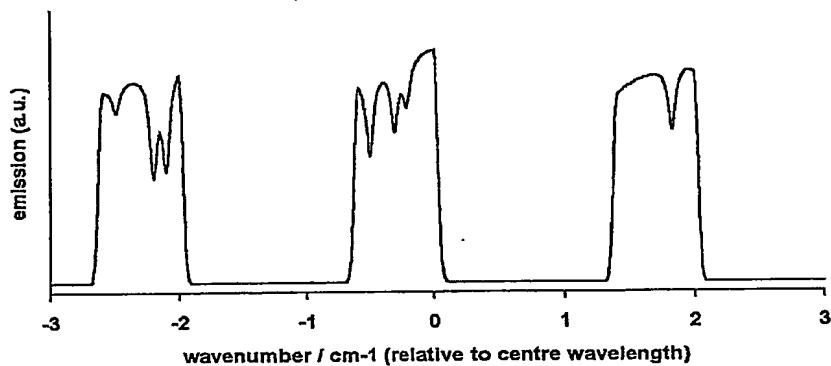


Figure 17b

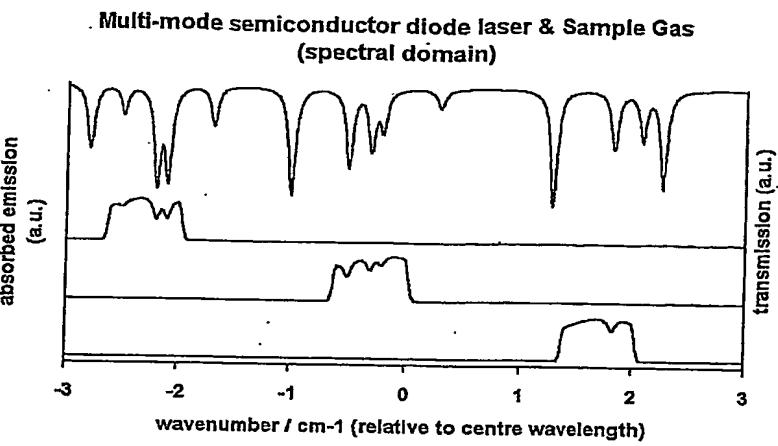


Figure 18

Multi-mode semiconductor diode laser & Sample Gas +
temp. tuning (spectral domain)

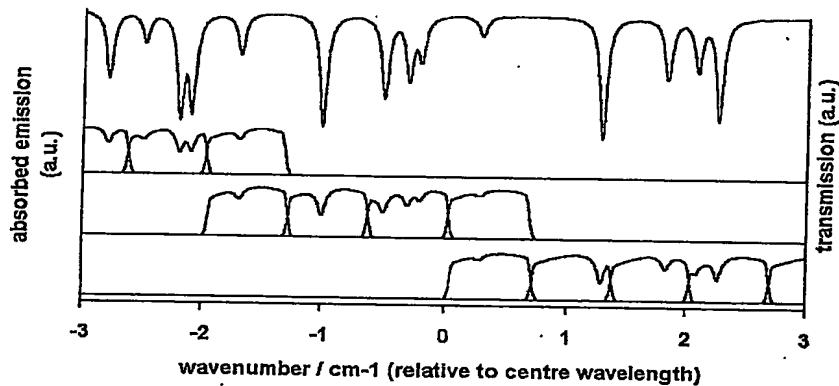
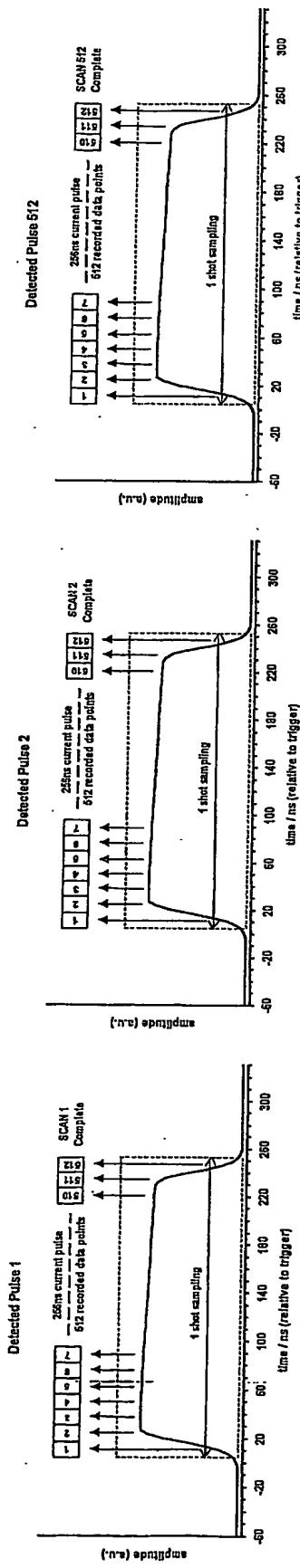
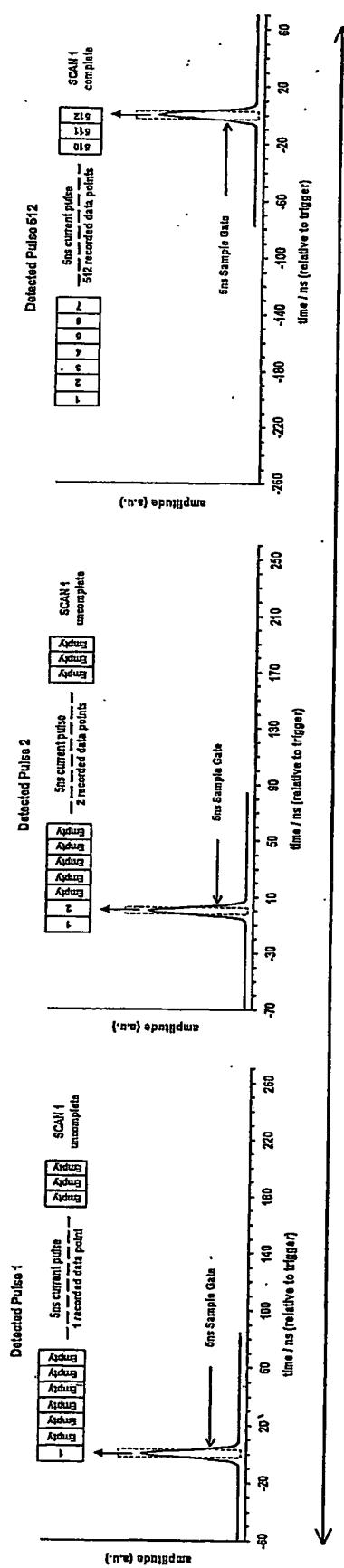


Figure 19

Method 1



Method 2



39.1 ms duration at 20KHz PRF

Figure 20

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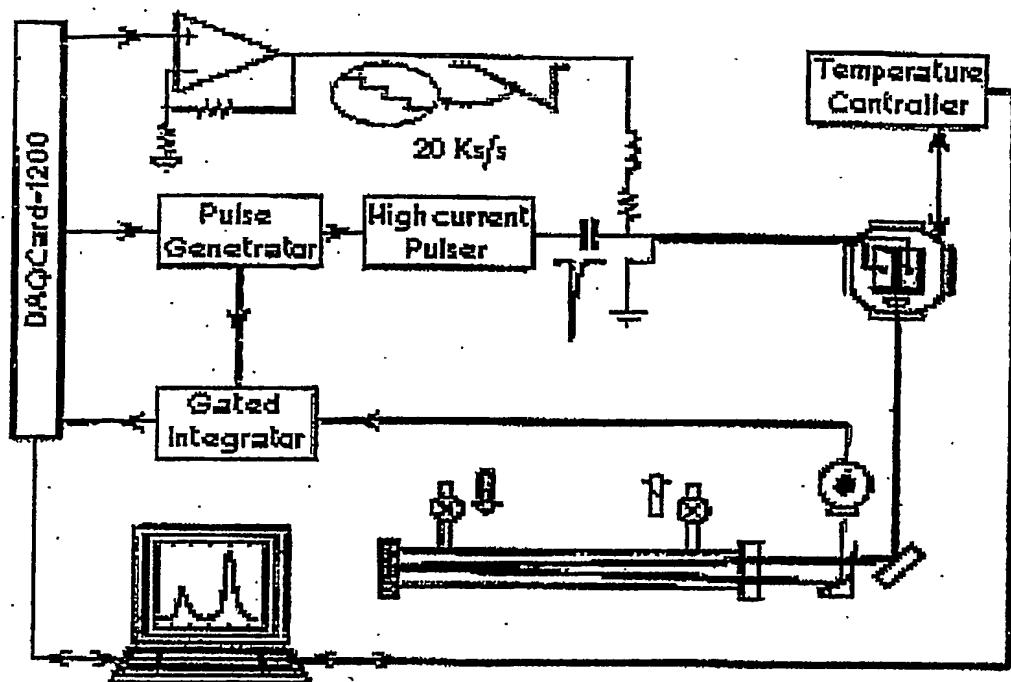


Figure 21

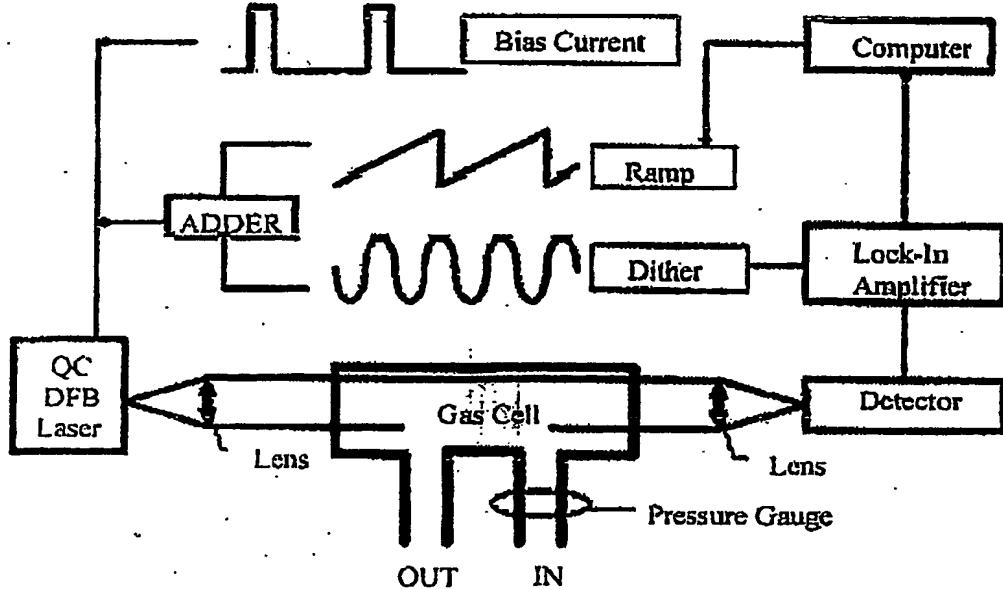


Figure 22

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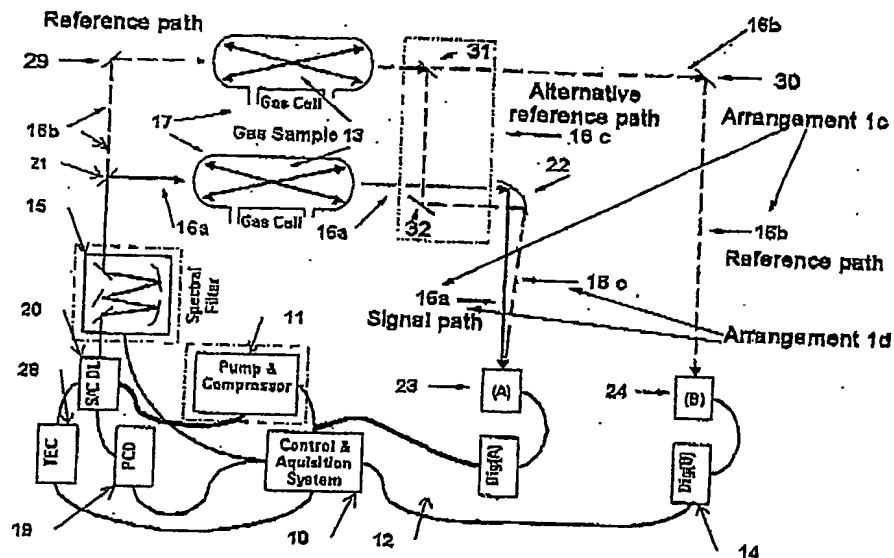
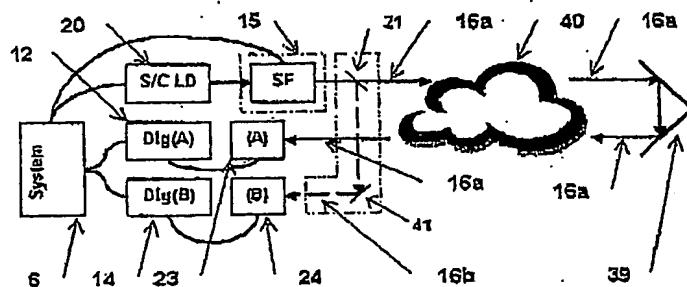


Figure 23

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Arrangement 1e



Arrangement 1 f

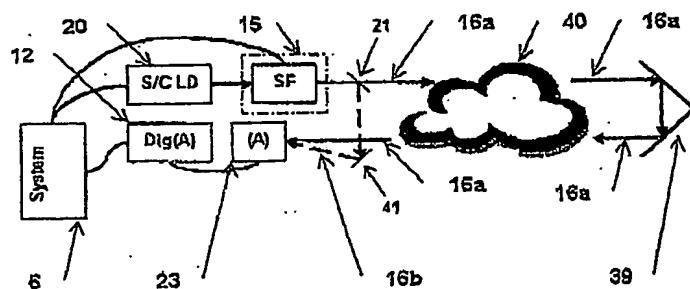


Figure 24

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